CERTIFICATION OF APPROVAL

EOR USING IONIC LIQUIDS

BY

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

_____

LAI YEN HUA

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Every effort has been made to identify, and make an appropriate citation to, the original sources. If there have been any accidental errors, or omissions, I apologize to those concerned.

Abstract

As the fact goes, oil is not a renewable energy. As this powerful source is gradually depleting, the demand to recover any single possible drop of the reserves is given serious concern. In conjunction, Enhanced Oil Recovery (EOR), which is a third stage of oil recovery that was carried out after secondary recovery, plays an important role in retrieving petroleum more efficiently. In improving the fluid flows, this project works on refining a compatible Ionic Liquids (ILs) in EOR applications. ILs are salts that are in liquid state below 100℃, composed wholly of anions and cations (Divya Nair G, Development of Ionic Liquids as a Novel EOR Agent Master Symposium, 2012). Studies show that long alkyl chain ionic liquids have the potential to decrease the interfacial tension (IFT) of n-alkanes. Reservoir oil residual will be mobilized if the capillary forces are reduced due to the reduction of IFT against crude oil. In this study, the characterization of ILs will be carried out after its synthesis. After that, the best synthesized ILs will be attempted and run for effectiveness of EOR by using core flood test.

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Abbreviations and Nomenclatures

D

DSC Differential Scanning Calorimetry

E

EOR Enhanced Oil Recovery

I

IFT Interfacial tension

IL(s) Ionic Liquid(s)

N

NMR Nuclear Magnetic Resonance (spectroscopy)

R

RF Recovery Factor (%)

T

TGA Thermogravity Analysis

TLC Thin Layer Chromatography

Chapter 1: Introduction

1.1 Background of Study

Enhanced Oil Recovery (EOR), which is a third stage of oil recovery that was carried out after secondary recovery, plays an important role in retrieving petroleum more efficiently. If truth be told, this technique can actually be initiated at any time during the productive life of an oil reservoir. Its purpose is not only to restore formation pressure, but also to improve oil displacement or fluid flow in the reservoir (Schlumberger).

In mobilizing the residual oil, reducing the capillary forces by reducing IFT against crude oil can achieve significant fluid flow performance. Acting as an active agents flooding into the oil reservoir, ILs based surfactant found to be more effective for higher saline formation water (Ali Zeinolabedini Hezavea, 2012). ILs are salts that are in liquid state below 100 ℃, composed wholly of anions and cations. In recent years, researches are developed to study the effectiveness of ELs as an EOR agent in flooding methods.

This research is aimed at showing the suitability of several ionic liquids as effective alternative for conventional surfactants in EOR. There are, however, a few limitations for the ILs to be operational. The conditions include the high pressure and high temperature of the reservoir, compatibility of ILs in saline environment, and potential of reducing IFT against crude oil in the reservoir. A relevant mobility property like viscosity, as well as density, can be experimentally done.

A novel ILs that were synthesized and characterized and being taken into measurement for this research (Divya Nair G, Development of Ionic Liquids as a Novel EOR Agent Master Symposium, 2012). The ionic liquids, [HMIM] [DOOS], [1-hexyl-3-methylimidazolium] [dioctysulfosuccinate], will be used to run the core flooding test.

1.2 Problem Statement

Given that the chemical flooding method can be very promising, apparently surfactant EOR is very costly. Despite the efficiency of surfactant in chemical flooding, concerns rises when it involves high cost of implying this technique. Hence, research on looking for another approach to this alternative is glooming a key interest. While producing additional option for EOR, there is a few requirements must be achieved to generate optimum production. Thus, the best set of ILs generated will be used to running for the core flooding test.

1.3 Objective

This research aims to study ILs as alternative approach agents in EOR, without overlooking the EOR's main purpose to recover high percentage of crude oil in reservoir. In short, the objectives of this study are as follows:

- To study the physical and chemical properties of the synthesized ionic liquids
- To investigate foremost of EOR application in ILs through IFT testing and core flooding test

1.4 Scope of Study

This project will cover the following:

1. Synthesis of desired ILs with low IFT.
2. Study of synthesized ILs characteristics with comprises:
    i. Thermogravimetry analysis
    ii. Densities and viscosities measurements
    iii. NMR and elemental analysis
3. Investigation on EOR applications.

Chapter 2: Literature Review

2.1 Enhanced Oil Recovery (EOR)

Enhanced Oil Recovery (EOR) is a third stage of oil recovery that was carried out after secondary recovery. Oil recovered by EOR technology has been defined as the incremental ultimate oil that can be economically recovered from a petroleum reservoir, in excess of that which can be economically recovered by conventional primary and secondary methods (R.J. Watts, 1989). Its purpose is not only to restore formation pressure, but also to improve oil displacement or fluid flow in the reservoir (Schlumberger). The tertiary recovery, also known as EOR, comprises of 3 major forms, namely thermal recovery, gas displacement and chemical flooding. The selection of optimal injection for each application depends mainly on reservoir conditions i.e. pressure, temperature, porosity, permeability, and fluid properties.

Firstly, thermal recovery applies heat to thinner the oil, making it easier to be extracted. The examples of this method are steam flood and in-situ combustion. Secondly, for gas injection, miscible floods and/or immiscible floods are using carbon dioxide, nitrogen, and/or hydrocarbons as solvents to recover of low-viscosity light crude oil (> 20 ° API gravity). On the other hand, chemical flooding uses polymers or surfactants to improve oil flow.

Although chemical flooding is one of the most efficient EOR methods, it is one of the most costly methods to be implemented. The main workout of this method is to decrease the IFT between injection slug and crude oil. In mobilizing the residual oil, reducing the capillary forces by reducing IFT against crude oil can achieve significant fluid flow performance.

2.2 Interfacial Tension (IFT)

Interfacial tension, IFT, is described as the measurement of imbalanced molecular forces at the interface between two liquid phases co-existing in equilibrium per unit length, results in a behavior analogous to an elastic sheet. The main forces involving in IFT are adhesive forces or tension between the liquid phase of one substance and another substance. The interaction occurs at the surfaces of the substances involved, that is at their interfaces. In this context, it measures the molecular interactions of the interfacial molecules.

In mobilizing the residual oil, surfactants are being brought into a significant role in reducing the capillary forces by reducing IFT against crude oil. This helps in increasing the production of considerable fluid flow. Acting as an active agents flooding into the oil reservoir, ionic liquids based surfactant found to be more effective for higher saline formation water (Ali Zeinolabedini Hezavea, 2012).

Surfactants, sometimes called surface active agents, are largely used in well treatment (Schechter, 1992). Low concentration of surfactants in aqueous solution is used in chemical flooding by injecting into the reservoir. This lowers the IFT between oil and water, and thus enhancing fluid flow of the oil trapped by letting the oil to be pulled out away by the flowing water. The surfactant viscosity should be high enough to decrease the water/oil mobility ratio.

However, despite the efficiency of surfactant in chemical flooding can be very promising, the concern of relatively high implementing cost highlights the considerations of selection of optimum injection (Sara Lago, 2012). Over the years, countless researches have been done on looking for another approach to this alternative. In addition to follow a line of investigation, recent finding shows the glooming interest in ionic liquids as another option for chemical flooding. Nevertheless, this new developed interest caught the attention in ionic liquids when it can easily achieve the surfactant EOR requirements.

2.3 Surfactants

Surfactants are used in almost every phase of well treatment. Practically every fluid injected into hydrocarbon-rich formations contains surfactants as an additive (Schechter, 1992). Few of the examples of their functions are to:

- stabilize oil and water emulsion, or, on contrary, break undesirable emulsion
- alter wettability
- increase solubility of oil in water

The unique properties of aqueous surfactant solutions credited to the existence of a hydrophilic head group and a hydrophobic chain (or tail) in the molecule. The polar or ionic head group normally interacts with an aqueous condition, in which case it is solvated via dipole-dipole interactions (Laurier L. Schramm, 2000). In EOR with surfactant flooding the hydrophilic head interacts with water molecules and the hydrophobic tail interacts with the residual oil. Thus, surfactants can form water-in-oil or oil-in-water emulsions (Pashley, R.M. and Karaman, M.E., 2004).

Surfactant flooding is injection of one or more liquid chemicals and surfactants. The injection effectively controls the phase behavior properties in the oil reservoir, thus mobilizing the trapped crude oil by lowering IFT between the injected liquid and the oil (Sandersen, 2012). Surfactants are added to decrease the IFT between oil and water.

Due to certain physical characteristics of the reservoir, such as adsorption to the rock and trapping of the fluid in the pore structure, there might be some significant losses of the surfactant. It is also essential to be alert of the high loss of surfactant, occurring as a result of adsorption and phase partitioning inside the reservoir. This is because surfactant systems are sensitive to high temperatures and high salinity. This leads to rations for creating surfactant systems that can withstand such conditions. Otherwise, alternatives for surfactant should be undergone investigation.

The optimization criterion in surfactant flooding is to maximize the amount of oil recovery, while minimizing the chemical cost. While it is necessary to reach low IFT for

the surfactant system, minimizing only the IFT may not always coincide with optimal oil recovery, as low IFT is not the only essential condition to meet in order to get a successful and efficient oil recovery (Fathi, 1984).

2.4 Ionic Liquids

Ionic liquids, ILs, are salts that are in liquid state below 100 ℃, wholly composed of cations and anions. Today, researches are developed to study the effectiveness of ILs as an EOR agent in flooding methods. Numerous studies prove that long alkyl chain ionic liquids are capable to lower the IFT of n-alkanes. With such, ILs have attracted much interest and gained acknowledgment as potential environmentally benign solvents due to some of their inimitable properties. These properties of ILs result from the composite properties of the wide variety of cations and anions. (Mustafizur Rahman, 2006)

Most of the ILs are liquid at room temperature and usually exhibit negligible vapor pressure, which reduces the possibility of air pollution and loss of materials at ambient conditions (John D. Holbrey, 2003). This is how ILs become one of the most popular 'green' media for chemists and engineers due to their superbly versatile physicochemical properties (Divya Nair G, Development of Ionic Liquids as a Novel EOR Agent Master Symposium, 2012). They have been studied as novel solvents for organic synthesis polymerization, and liquid-liquid extraction, in electrochemical studies (Zhiying Li, 2004), gas chromatography (Daniel W. Armstrong), and for catalysis (Zhongkui Zhao, 2005).

One of the distinctive applications of ILs is as novel EOR agent, as has been shown in a few earlier publications. Taking into account of the miscellaneous challenges associated with diverse traditional EOR agent, ILs hold prospects as alternative in the rapidly growing EOR. The reasons of choosing ILs to be the research subject matter are due to its properties i.e. the aggregation number can be controlled by changing the length and shape of the hydrocarbon tail, the type of polar head group, and/or the nature and size of the counter-ion. In other words, varying the cationic and anionic components in ILs can change their physical and chemical properties in a systematic manner.

Accordingly, this promising ILs can serve as new EOR options with important advantage of being non-volatile liquid over a wide temperature range. This paper shall discuss on the micellization in aqueous solutions of dialkylimidazolium ILs, as well as their mixtures with conventional surfactants. As mentioned earlier, ILs contain long alkyl chain of having hydrophilic imidazolium head group and hydrophobic tail. This unique characteristic allows ILs to act as a good option for surfactants. In this study, the synthesized IL, [HMIM] [DOSS] (Divya Nair G, Development of Ionic Liquids as a Novel EOR Agent Master Symposium, 2012), will be use to run the core flooding test, in order to test the recovery factor of the oil.

Chapter 3: Research Methodology

Research and experiments will be conducted in three systematic sections:

1. Ionic liquids syntheses
2. Ionic liquids characterization
3. Investigation of EOR applications

3.1 Ionic Liquids Synthesis

Ionic liquids are generally synthesized by a quaternization reaction of amines, N-heterocycles, or phosphines with alkyl halides in an *SN2* type reaction similar to *Figure 1*. If another anion is desired than that formed in the quaternization step, an anion exchange can be performed with the corresponding acid or salt (Sylvia O. Nwosu, 2009).

Figure 1 Synthesis of 1-hexyl-3-methylimidazolium bromide

Large solvent effects on the kinetic rate are observed with the qualitative trend that rate increases with increasing solvent "polarity". Reactions involving ionic liquid synthesis are highly exothermic, and require adequate heat removal or a solvent or both. A solvent is also useful as some ILs or their intermediates are actually higher melting-point solids or viscous liquids, which would require much different processing techniques.

The syntheses of ILs are segregated into two distinctive sections:

i. Quaternization
ii. Metathesis

3.1.1 Theoretical Calculation

Calculations are done before the experiment was conducted to ensure sufficient yield of more than 10g of ionic liquids is achievable. Basic equations to calculate mole, mass, volume and density are applied with a basic assumption of equimolar reaction of 1 to 1 mole.

3.1.2 Quaternization

These steps form the cation of the ionic liquid, the synthesis of 1-hexyl-3-methylimizazolium bromide.

1. A 100 ml 3-headed round-bottomed flask is flushed with dry nitrogen. The apparatus is set on the reflux heater and conducted in fume chamber.
2. The reflux heater is configured with thermocouple set up for temperature measurement and it is dipped inside the oil bath. A test run is done before starting the experiment.
3. A 12 ml syringe is used to charge methylimizadole into the 3-headed round bottomed flask at the rubber stopper.
4. Then, 1-bromohexane is added to the flask slowly using the 12 ml syringe. This is to avoid vigorous smoke release.
5. The solution is then heated under reflux and under nitrogen atmosphere at 70℃ and 800 rpm for 48 hours. Nitrogen is set to flow at 10 cc/min air and 85 bar.
6. The magnet stirrer is observed and the speed is increased to 800 rpm to 1100rpm gradually.
7. After 48 hours, the reflux heater is stopped and the solution is cooled down to room temperature.
8. Next, the solution is washed with 15ml of ethyl acetate for 3 times. The washing is done by shaking the mixture manually until the clear ethyl acetate solution turns cloudy.
9. Step 8 is repeated using 15 ml of diethyl ether.
10. Finally, the washed solution is dried in a vacuum line at 70℃ for 72 hours.

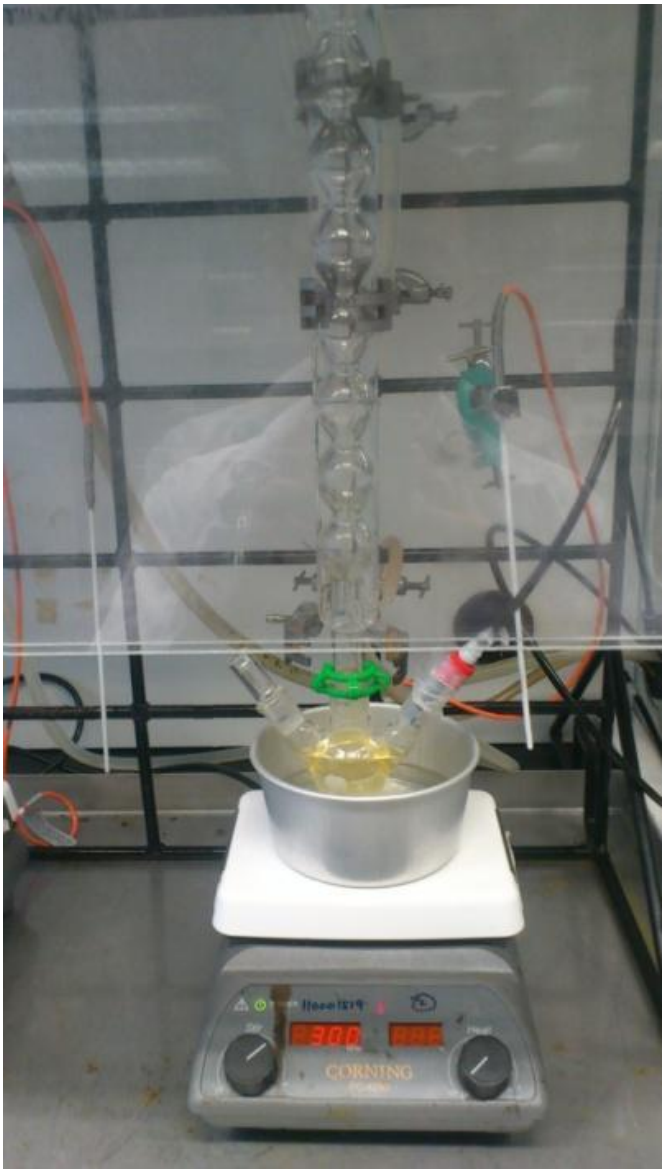


Figure 2 Reflux Heater

Figure 3 Quatenization of 1-hexyl-3-methylimidazolium bromide

3.1.3 Metathesis

Quaternization process continues with metathesis. The process is continue with these steps.

1. 1-hexyl-3-methylimizazolium bromide is mixed in 50 ml of acetone using a 100ml Erlenmeyer flask and stirred with a magnetic stirrer until it dissolves completely.
2. An equimolar amount of sodium dioctylsulfosuccinate is handled in a similar manner as step 1.
3. Both the mixture are then combined and stirred at room temperature for 30 minutes.
4. The solution is filtered using a filter paper and the solid precipitate (NaBr) is removed.
5. Next, the solution is heated using Rotary Evaporator at 65 ℃ to remove volatile solvent for 30 minutes.
6. The moisture from the compound is removed under vacuum line at 65 ℃ for 24 hours.
7. Finally, the remaining solvent is removed under vacuum oven at 70 ℃ for 48 hours to get [HMIM][DOSS].

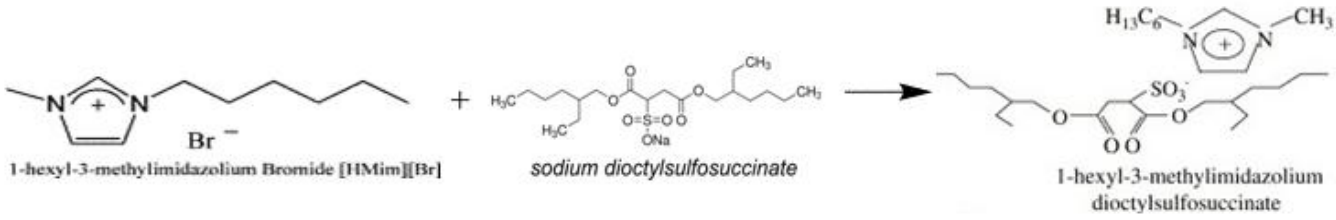


Figure 4 Metathesis of [HMIM][DOSS]

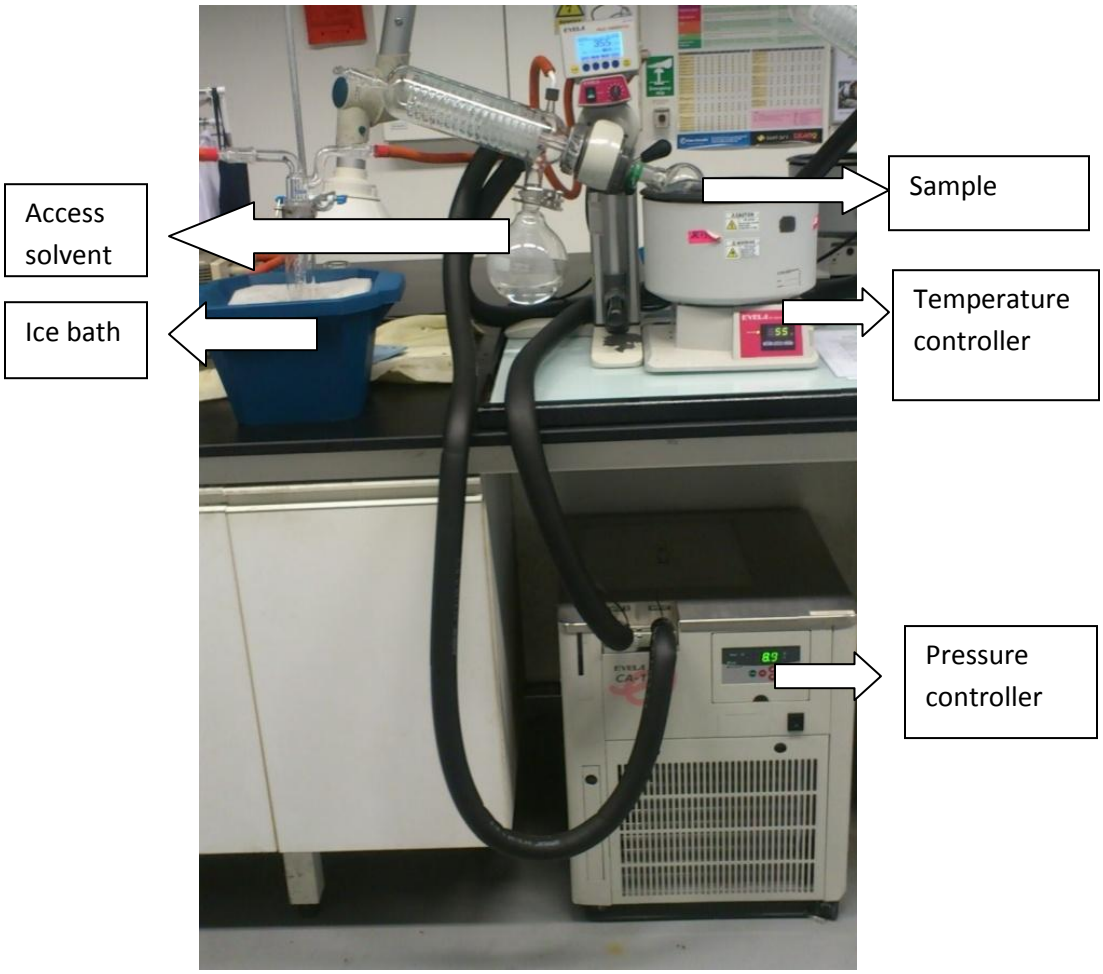


Figure 5 Rotary Evaporator

3.2 Ionic Liquids Characterization

Syntheses of ILs required careful observations and detailed analysis in order to further study its suitability as alternative EOR agents. A few analyses will be done to study the physical and chemical properties of ILs.

3.2.1 Water Content

Coulometric Karl Fisher titrator DL39 (mettle Toledo) is used to analyze the water content of the synthesized ionic liquid. Measurements were repeated a few times to get an average value for better accuracy.

3.2.2 Thermogravity Analysis

The decomposition temperature of the synthesized ionic liquid is measured using Perkin-Elmer, Pyris V-3.81 whereby the sample is positioned in aluminium pans under nitrogen atmosphere at a heating rate of 10 ℃/min.

3.3.3 Density and Viscosity Measurements

To measure the density and viscosity of the synthesized ionic liquid, Stabinger viscometer (Anton-Paar model SVM3000) is used within a temperature of range of 293.25K to 353.15K.

3.3.4 NMR Analysis

Shimadzu FTIR-8400S spectrometer with $4cm^{-1}$ resolution with a wave number range of 350 to 7800 cm^{-1} is used. H NMR spectra is taken in $CDCI_3$ solvent and recorded on a BrukerAvance 300 spectrometer and CHNS-932 (LECO instruments) elemental analyzer is used for ether functionalized ionic liquid characterization.

3.3 Investigation of EOR Applications

The synthesized IL is being measured against Dulang crude oil for IFT. Different set of concentrations will be studies in order to determine the optimum result produced. After the previous steps are done, the best IL concentration will be used to test the applicability to be used as EOR agents. This step is completed by running the IL using core flooding test.

The parameters used for core flooding would be at the following:

- Temperature = 85 ℃
- Pressure = 1500psi
- Injection rate = 0.3 cc/min

3.4 GANTT Chart

Table 1 Final Year Project 1 (JAN 2013) proposed activities timeline

No.	Details/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Topic Selection		•												
2	Submission of Extended Proposal						•								
3	Proposal Defense Presentation Preparation								•	•					
4	Experimental work										•	•	•		
5	Interim Report Submission													•	•

Table 2 Final Year Project II (May 2013) proposed activities timeline

No.	Details/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work Continues	•	•	•	•	•	•	•	•						
2	Submission of Progress Report								•						
3	Project Work Continues								•	•	•	•	•	•	•
4	Pre-SEDEX													•	
5	Submission of Final Draft											•			
6	Submission of Technical Paper											•			
7	Oral Presentation														•
8	Submission of Project Dissertation (Hard Bound)														•

Chapter 4: Results & Discussion

4.1 Ionic Liquids' Synthesis

4.1.1 Calculation

Table 3 Data for Quaternization Process

Chemical	**MW (g/mol)**	**Density (g/cm^3)**	**Boiling Point (℃)**	**Amount (moles)**	**Volume (ml)**	**Mass (g)**
1-Methylimidazole	82.10	1.030	198	0.05	3.99	4.11
1-Bromohexane	165.07	1.276	154	0.06	7.76	9.90

The values in *Table 3* above are decided on the assumption that the reaction is equimolar with an excess of 0.01 moles of 1-bromohexane, taking 1-methylimidazole as the limiting reagent. The equations used are as below:

$$\rho = M/V$$

$$\text{mole} = m/MW = \rho V / MW$$

where

ρ = density g/cm^3

m = mass, g

V = volume, mL

MW = molecular weight

4.1.2 Observation & Discussion

Before starting the experiments, the thermocouple sensor is checked to ensure it is at all time dipped into the oil bath, so the temperature measured reflects the correct value shown on the screen. If this is not done correctly, heating process on the oil bath will not stop, this may cause fire. This is shown in *Figure 6* below.

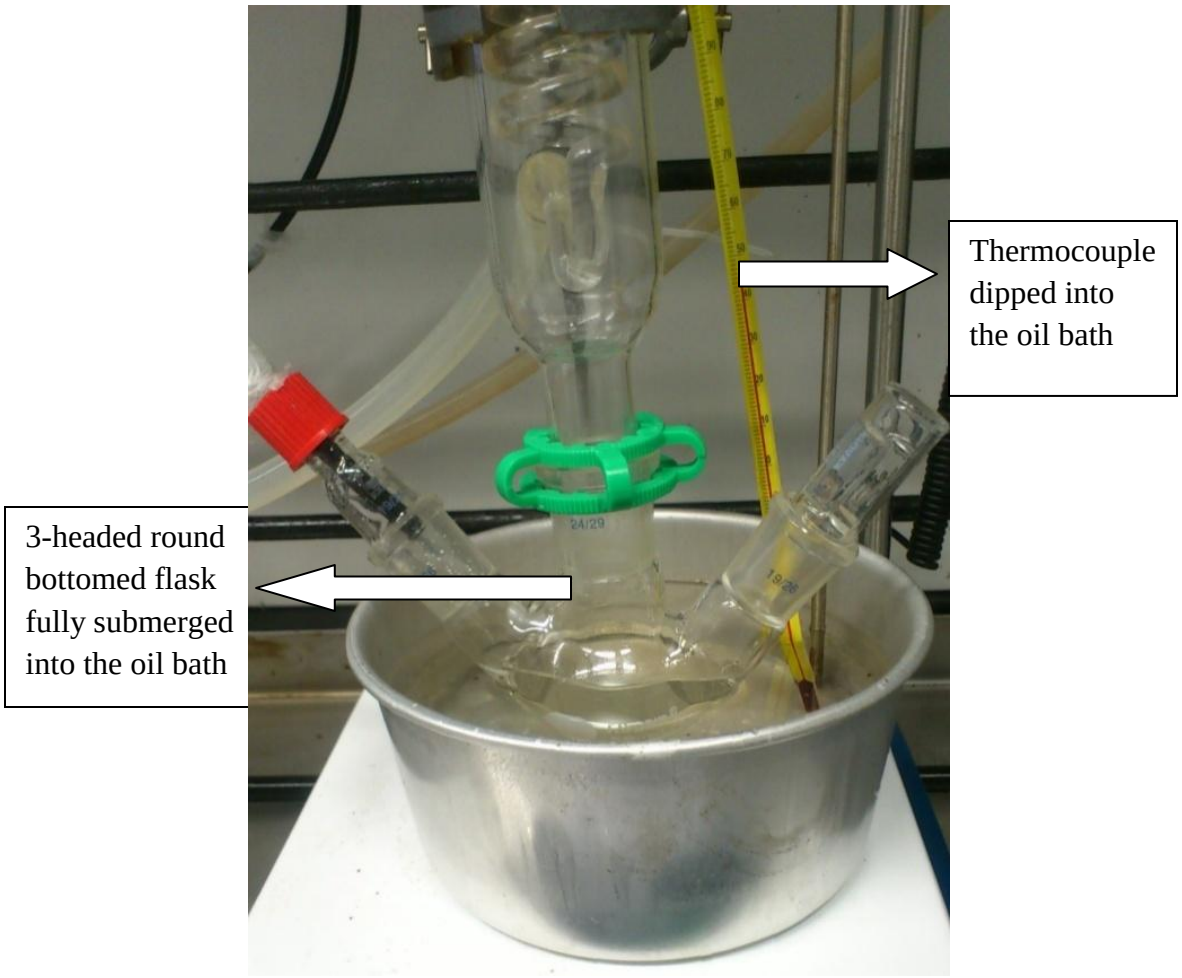


Figure 6 Oil bath of [HMIM][Br]

While mixing 1-methylimidazole with 1-bromohexane, 1-bromohexane is slowly added into the flask to avoid vigorous smoke as the reaction is exothermic. The 3-headed round bottomed flask with the chemical solution has to be fully submerged into the oil. This is to ensure the constant temperature distribution. The stirring speed is increased gradually as more force is needed to stir the solution when the reaction creates a more viscous solution.

In the beginning, an excess of 0.01 mole of 1-bromohexane is being used to carry out the study, while 1-methylimidazole is acting as the limiting reagent. The reason is to ensure that all of the 1-methlylimidazole is completely reacted. The quaternization process takes two days to complete.

The study is carried out using a reflux heater to heat the reactants while continually cooling the vapour to be returned back to the flask as liquid. The reaction is also carried out under nitrogen atmosphere to ensure that the air is inert and no loss of solvent occurs through constant evaporation.

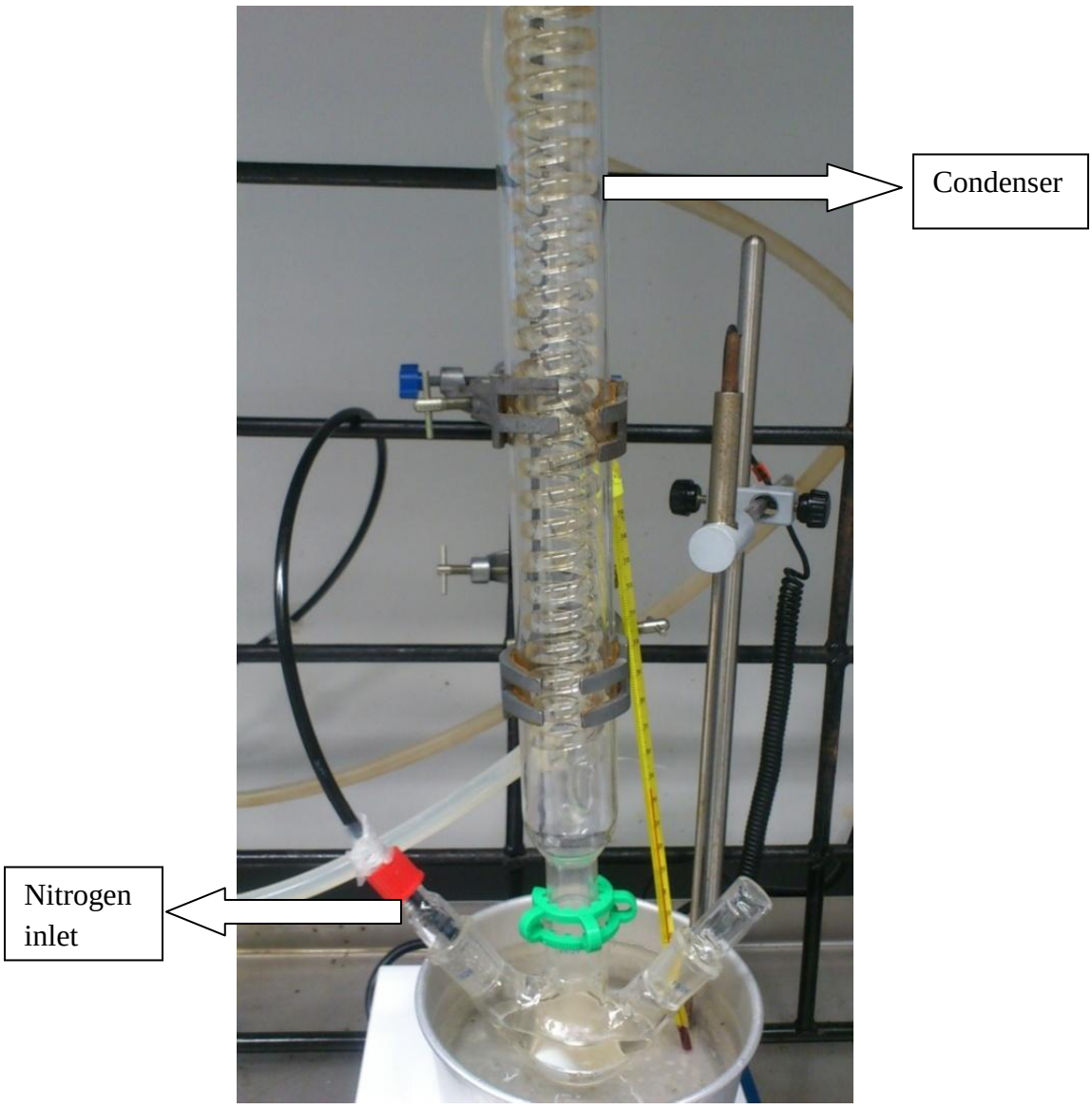


Figure 7 Reflux heater

Observation indicates the both the 1-methylimidazole and 1-bromohexane are colourless. However, the end product of quaternization is also a colourless liquid. The product is found out to be viscous. In order to know if the quaternization process has completed, TLC is carried out. Two spots are being observed at two different levels on the plate, indicates that the reaction is completed. This can be shown in *Figure 8* below.

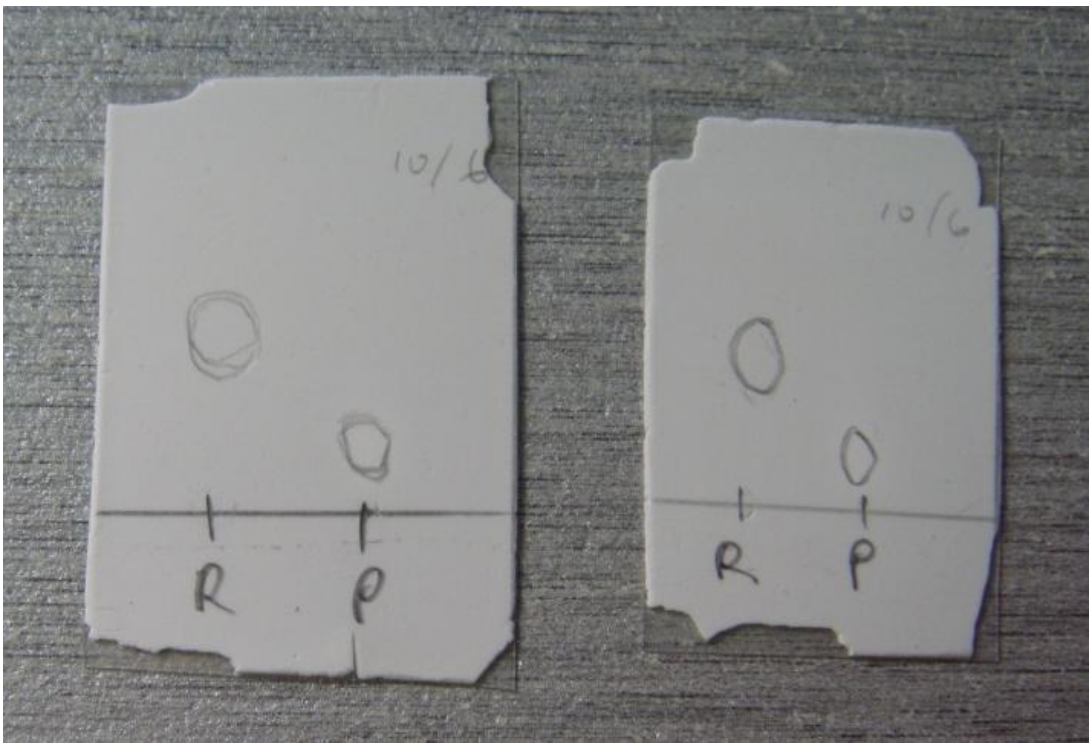


Figure 8 Two spots on TLC analysis

Washing the products after the reaction is essential to get rid of the access reactants. The products turn from colourless to cloudy after washing. If there is any access reactant, two layers of liquid is formed. The mixture will not mix due to the different densities of the products and the solvent. However, only one layer of solution is being observed after the washing. The possible reason is that all the reactants have been completely reacted, leaving no access reactants.

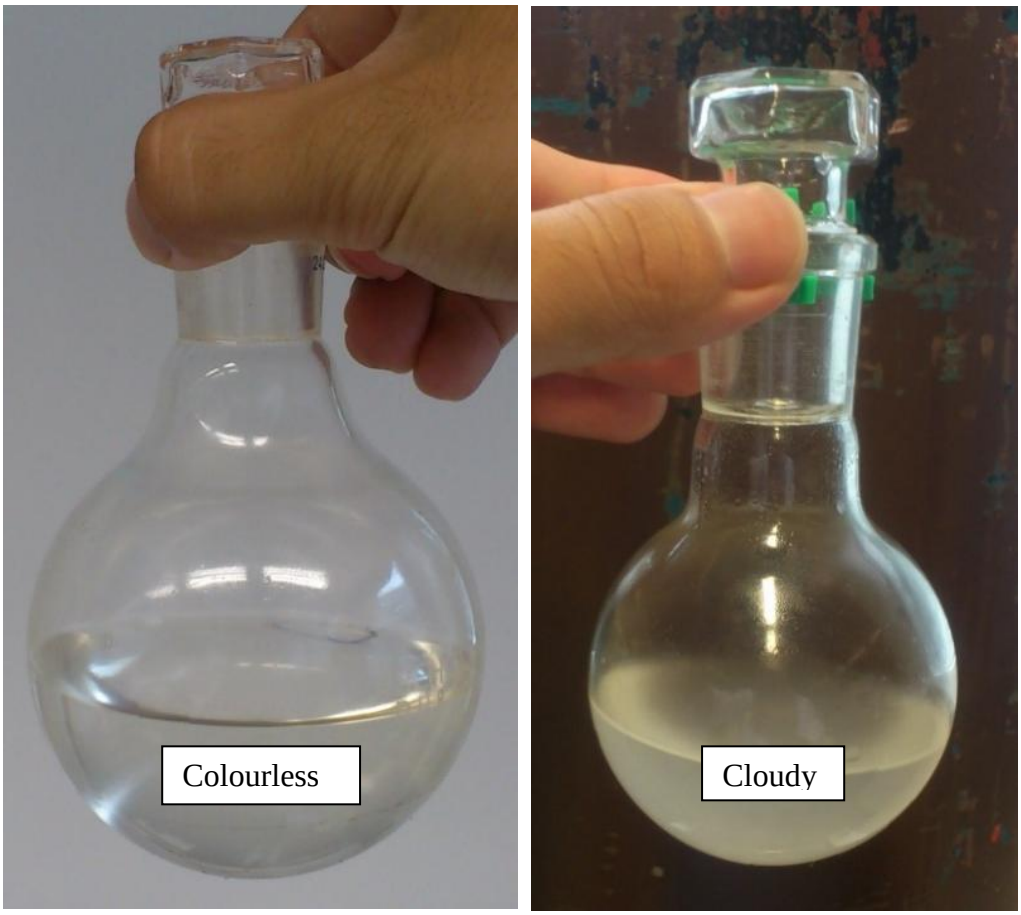


Figure 9 Washing of [HMIM][Br]

As shown in *Figure 9*, the graphics on the left shows the physical properties of the solution before washing, and the graphics on the right shows the appearance of the solution after washing.

The product is the placed in the Rotary Evaporator to remove the solvent. To confirm the structure of the products, the sample is sent for NMR analysis. The chemical is found to be more viscous and colourless after taken out from Rotary Evaporator, as the volatile solvent has been removed. Next, the moisture from the compound is removed under vacuum line. Finally, the remaining solvent is removed under vacuum oven for 48 hours to get [HMIM][Br].

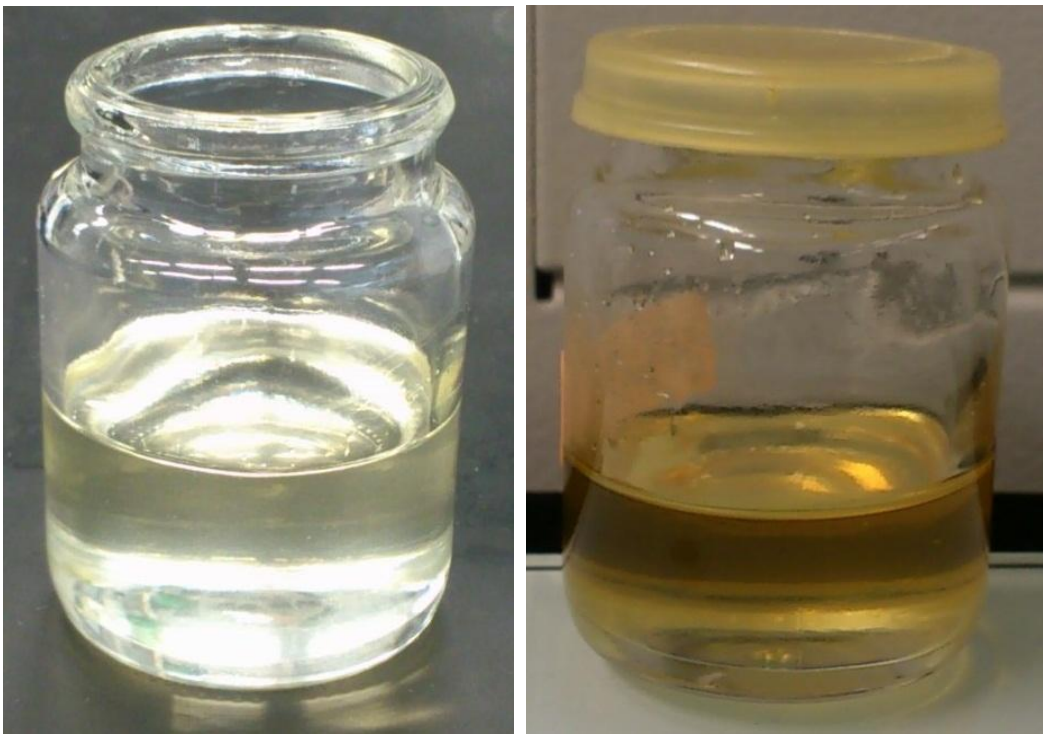


Figure 10 [HMIM][Br] before and after vacuum oven

After vacuum oven, most of the remaining solvent is being removed. This is the explanation of the change in colour of the chemical from colourless white into yellowish liquid. Apparently, besides the colour, the chemical appears to be more viscous. The comparison is very obvious, as shown in *Figure 10* above.

Metathesis of [HMIM][Br] and [Na][DOSS] is conducted at room temperature for 30 minutes. Initially, both the components are mixed separately in acetone as an intermediate solvent. It is essential to use solvent to mix with [Na][DOSS] because it is in solid state in room temperature.

Due to the high volatility of acetone, the flask has to be closed when carrying out the mixing of the chemical solution. This is to avoid the loss of the sample. The reactions are equimolar. Filter paper is being used to filtrate the solid precipitate as the reaction produces solid precipitation. The white solid precipitate is NaBr with no odour. This can be seen in *Figure 11*, the solid precipitate, NaBr.

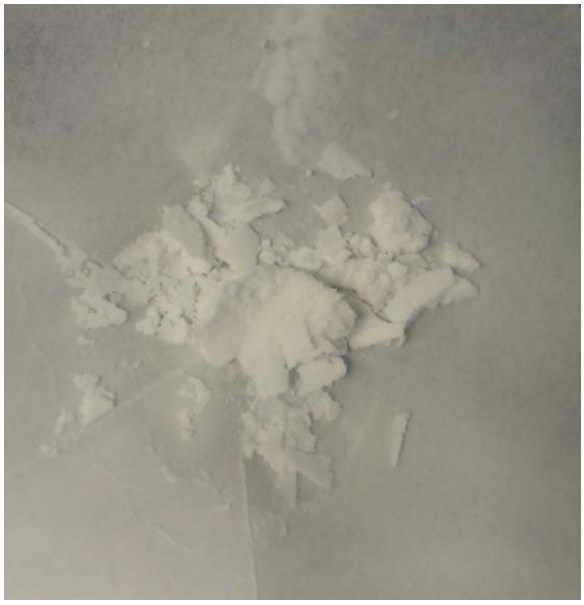
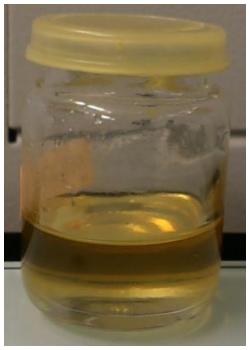


Figure 11 Solid precipitate, NaBr

The purified product is placed in the Rotary Evaporator to remove the solvent acetone. Temperature of 65 ℃ is set for water bath as the boiling point of the solvent is 56 ℃. The process takes about 60 minutes to complete before proceeding to the vacuum oven. The products are dried under the vacuum oven for 72 hours at 70 ℃.

Figure 12 Vacuum Oven

Table 4 Final product

Chemical	Sample	Colour	Physical State	Yield (g)
[HMIM][Br]		Yellow	Viscous	11.332
[HMIM][DOSS]		Light yellow	Viscous	11.269

4.2 Physical and Chemical Properties Analysis of Ionic Liquids

4.2.1 Thin Layer Chromatography

Thin layer chromatography, TLC, is among the most useful tools for following the progress of organic chemical reactions.

TLC is performed on a sheet of plastic, coated with a thin layer of adsorbent material, which is also known as the stationary phase. The product sample is deposited as a spot on the stationary phase. At the same time, another spot of constituents of sample is deposited on the same level, in this study, it is 1-methylimidazole. The bottom edge of the plate is placed in a solvent, which its function is to move up the plate by capillary

action. As soon as the solvent reaches the other top edge, the plate is removed from the solvent.

Two spots can be detected on the plate. Irradiation of the plate with ultraviolet light will permit location of the spots of compounds that fluoresce. However, the spots cannot be observed under the UV light. This is due to the reason that the chemicals absorb UV light and do not fluoresce. However, the black spots appear against the fluorescing background. Since these spots usually fade, it is a good idea to circle the spots with a pencil while they are still visible in order to have a permanent record of the chromatogram.

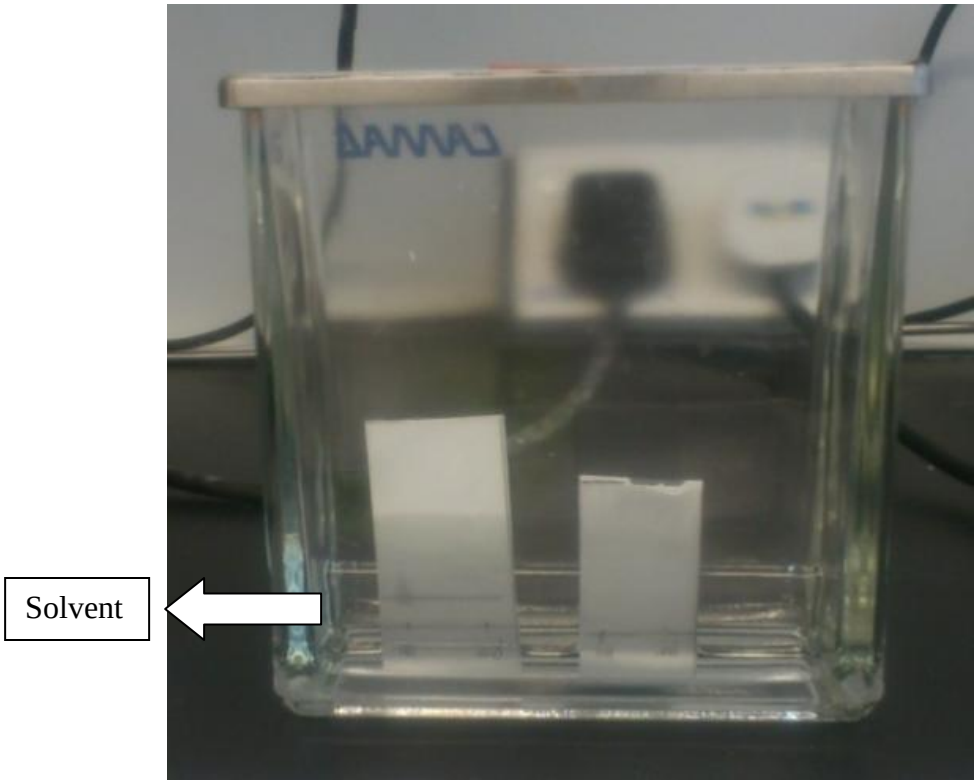


Figure 13 TLC in container

4.2.2 Water Content

Table 5 Water Content of [HMIM][DOSS]

Ionic Liquid	Water Content, ppm		
[HMIM][DOSS]	**Trial 1**	**Trial 2**	**Average**
	7236.513	5972.406	6604.4595

Theoretically, most of the ionic liquids have the common range of water content, which is happened to be in between 100 ppm to 1000 ppm. However, the experimental data shows that the product contains very high water and it is very far deviated from the theoretical range. This might due to the reason that the sample was exposed to atmospheric moisture for a long time. Thus, the sample needs to be put in the vacuum line and vacuum oven for a longer time.

Figure 14 Karl Fisher Titration

4.2.3 IFT Analysis

IFT test is being carried out. The result can be seen from the *Table 6*. The low IFT value of IL is able to reduce the surface tension between the oil and the rock. Consequently, it can change the wettability of reservoir from oil wet to water wet, and hence improve oil recovery.

Table 6 Properties of 4000ppm [HMIM][DOSS]

Density, g/cm^3	0.9921
IFT, nM/m	0.3200

4.2.4 Thermogravity Analysis

Thermogrativy analysis, TGA, is performed on samples to determine changes in weight in relation to change in temperature.

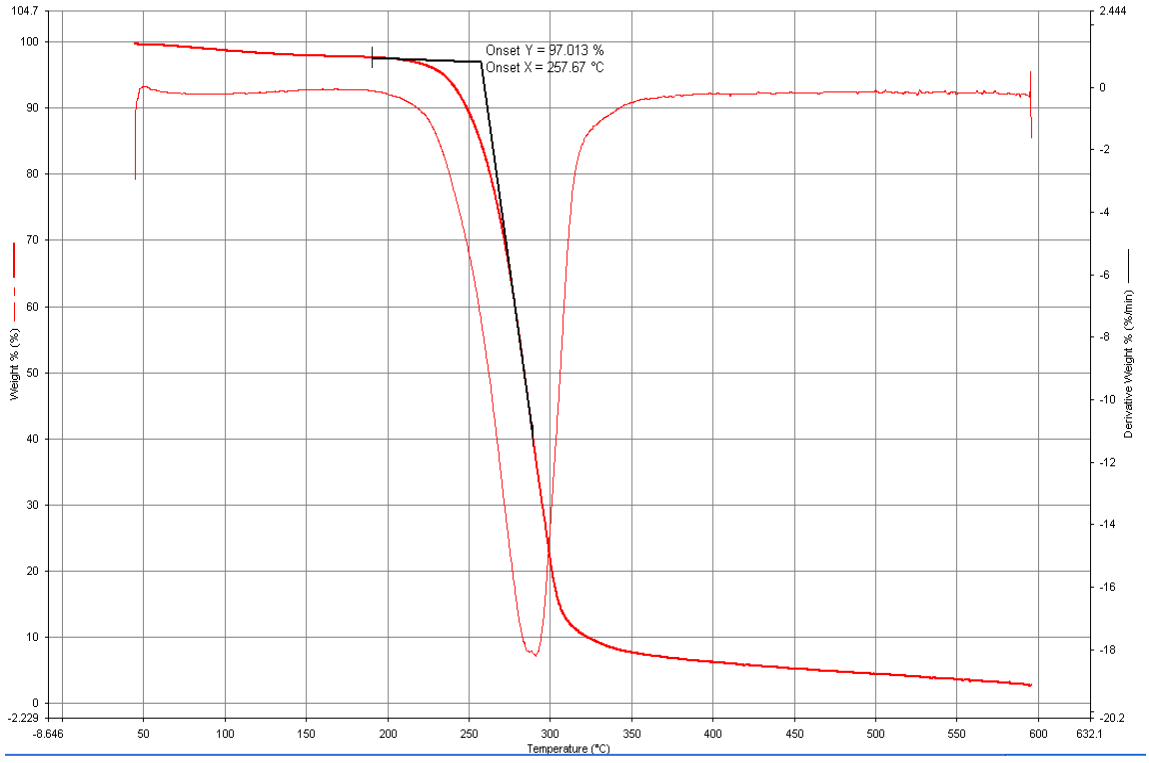


Figure 15 TGA for [HMIM][DOSS]

The TGA in *Figure 15* shows that [HMIM][DOSS] decomposes at 257.67 ℃. From the figure, it clearly shows that [HMIM][DOSS] is pure and free from any starting material. The IL is thermally stable up to 257.67 ℃ with complete decomposition 335 ℃. This high thermal stability is suitable to be used as an EOR agent.

4.2.5 Differential Scanning Calorimetry

The sample is being sent for DSC test. The differential scanning calorimeter (DSC) is a fundamental tool in thermal analysis. It is functionalized to understand amorphous and crystalline behavior, polymorph and eutectic transitions. The result can be shown in the *Figure 16*. From *Figure 16* shown, there is no transition state.

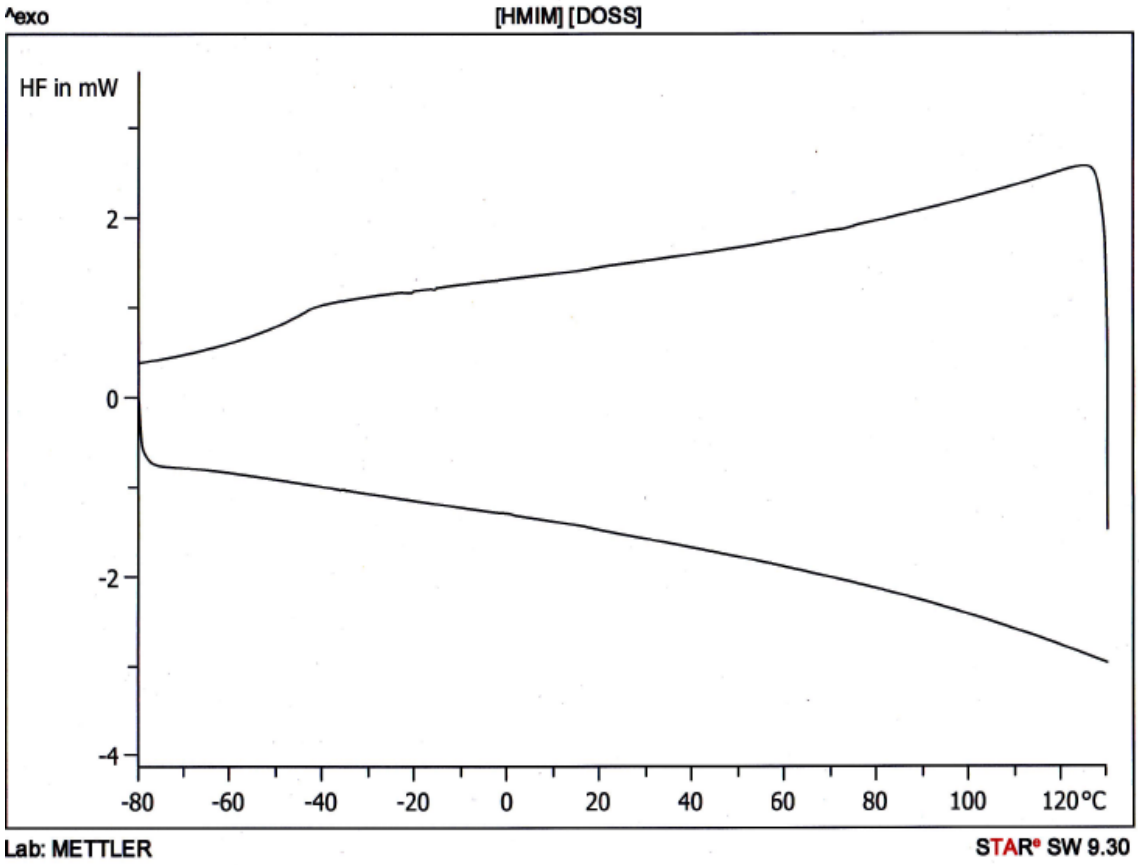


Figure 16 DSC

4.3 Ionic Liquids for EOR Application

The next step would be the attempt to test the application of EOR using the synthesized ionic liquids. However, there are some properties of the core must be determined before hand, for instances porosity and permeability.

4.3.1 Core Properties

Some essential information is needed in order to find out the porosity and permeability of a core, for instances, length, diameter and weight of the core. To get an accurate value of measurements, digital caliper is being used. Accuracy of the digital caliper is 0.01mm. The *Figure 17* shows the digital caliper provided in the lab.

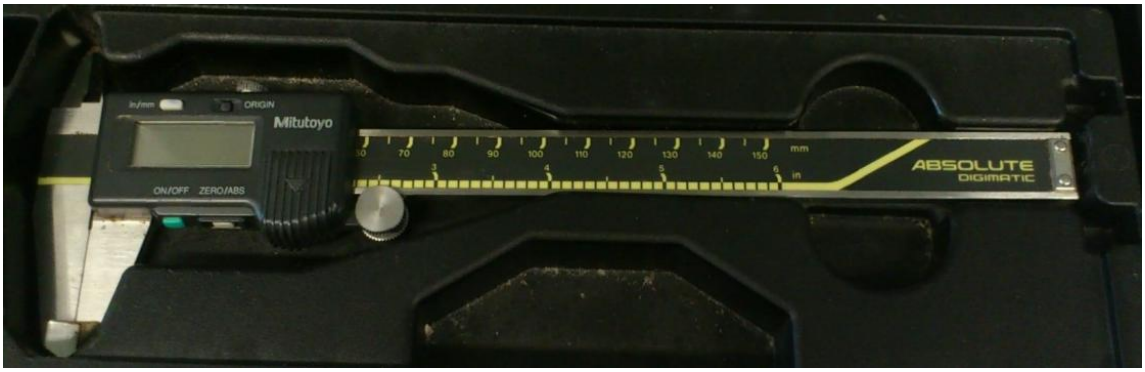


Figure 17 Digital Caliper

Upon obtaining the measurement, the basic properties of the core are porosity and permeability can be obtained by using the equipment provided in the lab. Porosity is the percentage of void space within a rock that can hold fluid, whereas permeability is the measurement of the ability of the rock to transmit fluids.

In the EOR lab, porosity and permeability can be measured using the equipment POROPERM Coval 30. Three cores from Berea Sandstone were used for the study. The POROPERM instrument is a permeameter and porosimeter used to determine properties of plug sized core samples at 400 psi confining pressure. In addition to the direct properties measurement, the instrument offers reporting and calculation facilities. Some of the measured data are as shown in the *Table 7*.

Table 7 Measurements of POROPERM Coval 30

Core Name	ONG	Core 2	Nicole 2
Porosity, %	14.81	18.736	17.058
Bulk Volume, cc	78.907	72.843	80.174
Grain Density, g/cc	2.531	2.637	2.599
Grain Volume, cc	67.221	59.195	66.498
Pore Volume, cc	11.686	13.648	13.676
K_{air}, mD	8.927	118.33	88.688
Bulk Density, g/cc	5.013	2.143	2.155

From the table shown, it is found out that the permeability, K, for Core ONG is only 8.927mD, which is unreasonable low. One of the possibilities of this low value is that the core is spoiled. Besides, it may be due to the reason that the core is filled with some fluids. Thus, this core is not been used for the study. The *Figure 18* shows the core samples taken for the analysis.

Figure 18 Core Samples

Theoretically, the equation used to get the core properties are as follow:

Pore Volume = Weight of wet core – Weight of dry core

Wet core is obtained by soaking the core with brine. Eventually the core will be saturated with brine when the fluid filled up the pore space within the core. When the core is filled with brine, the weight can represent the volume of the space taken up.

After the value of pore volume is being obtained, porosity can be calculated using the formula

$$\boldsymbol{Porosity\ \varphi = \frac{Pore\ Volume}{Bulk\ Volume}}$$

To measure the permeability in the lab, dry gas like N_2 is usually being used because of its convenience, availability, while minimizing fluid-rock reaction. The measurement of the permeability should be restricted to the low (laminar/viscous) flow rate region, where the pressure remains proportional to flow rate within the experimental error. At low pressures, it is assumed that the gases follow the ideal gas law.

Compared to the permeability value measured using liquid and the value with gas measurement, air perm is usually a little higher than liquid perm. It is discovered that permeability measurements made with air as the flowing fluid showed different results from permeability measurements made with a liquid as the flowing fluid. Air permeability is always greater than the permeability obtained when a liquid is the flowing fluid. On the basis of the laboratory experiments, liquids had a zero velocity at the sand grain surface, while gases exhibited some finite velocity at the sand grain surface (slippage). This slippage, results in a higher flow rate for the gas at a given pressure differential. Thus, the Klinkenberg correction is used to reduce air perm to an equivalent liquid perm.

The *Figure 19* shows POROPERM Coval 30 used to get porosity and permeability of the cores.

Figure 19 POROPERM Coval 30

4.3.2 Core Flooding: Restore to Original Reservoir Condition

Both the *Core 2* and *Nicole 2* cores are being saturated with brine water in glass desiccators. The glass desiccator is equipped with a vacuum pump. The set up can be shown in the *Figure 20*.

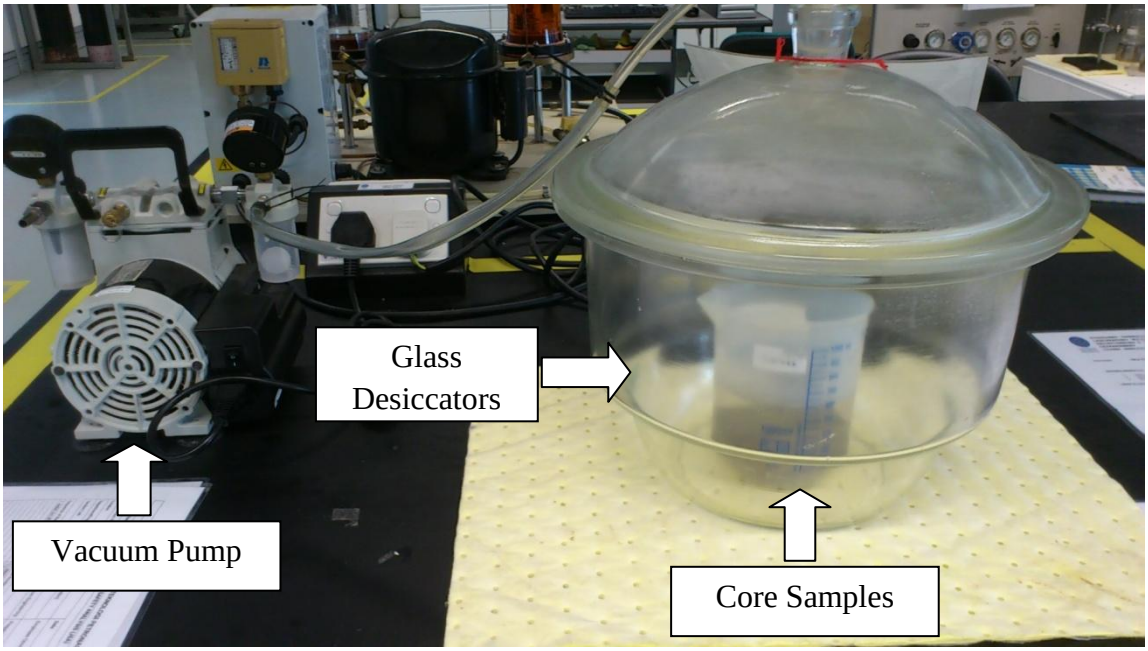


Figure 20 Glass desiccators with vacuum pump

It can be observed that bubbles are releasing from the core when the vacuum pump is turned on. This is due to the reason that the pore spaces inside the core is being sucked out and displaced by the brine water. The core samples are saturated for at least six hours. This is to ensure the core samples are fully and completely saturated with brine. While carrying this step, the glass had to be ensured that it is securely confined. This is to make sure that no air is entering the container and the vacuum pump can work well.

After the core samples are completely saturated with brine, the next step will be core flooding. Before the core flooding test is run for oil recovery factor, it is required to restore the core to original reservoir condition. This is done by flooding the saturated core with oil. The oil being used is Dulang oil. The *Table 7* shows the result of oil flooding with *Core 2*.

Table 8 Oil Flooding Data

Pore volume	13.648	cc
Initial Oil Volume (measure volume of water produced after oil flood)	12	cc
S_{wi}	12.075	%
S_{oi}	87.925	%

While injecting the saturated core with oil, then outlet from the core flooding produces 12ml of brine water. The amount of water being displaced will be equal to the amount of oil being retained in the pore. While 12ml of brine water is being displaced, this indicates that there is 12ml of oil being restored in the core sample.

Judging from the lab data as sorted in *Table 8*, the initial properties restored of the core is having 13.648cc of pore volume, while having initial oil volume of 12cc. This result indicates that the core is having initial oil saturation, S_{oi} of 87.925% and initial water saturation, S_{wi} of 12.075%.

4.3.3 Core Flooding: Secondary Flooding

Upon restoring the core to initial reservoir condition, the study proceeds with secondary flooding to determine the recovery factor. Brine is being injected while the amount of oil produced is being observed and recorded. Secondary flooding ended when no more oil is being produced. The core flooding equipment can be shown in *Figure 21* and the results can be seen in *Table 9*.

Table 9 Secondary Flooding

Volume of oil produced	3.97	cc
Residual Oil Volume	8.03	cc
Residual oil saturation	66.197	%
Secondary Oil Recovery	33.083	%

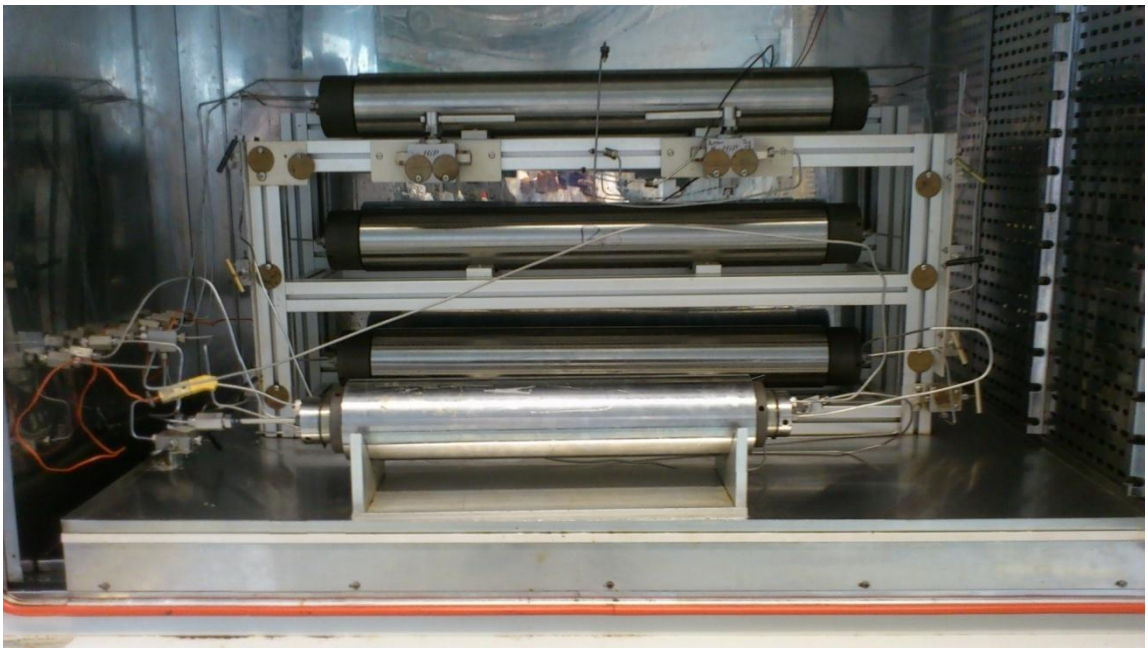


Figure 21 Relative Permeability Test System

4.3.4 Core Flooding: Tertiary Flooding

The secondary flooding ended when no more oil is being produced. To run tertiary flooding, the synthesized ionic liquid [HMIM][DOSS] is being used for injection. The result of tertiary flooding is being tabulated as shown in *Table 10*.

Table 10 Tertiary Flooding

Volume of oil produced	1.5	cc
Tertiary oil recovery	12.500	%
Total oil recovery	45.583	%

During the whole core flooding test, all the pressure is being monitored. The overburden pressure should be higher than the inlet pressure at all time. This is to ensure there is no leakage from the core during the injection. This can be shown in *Figure 22*.

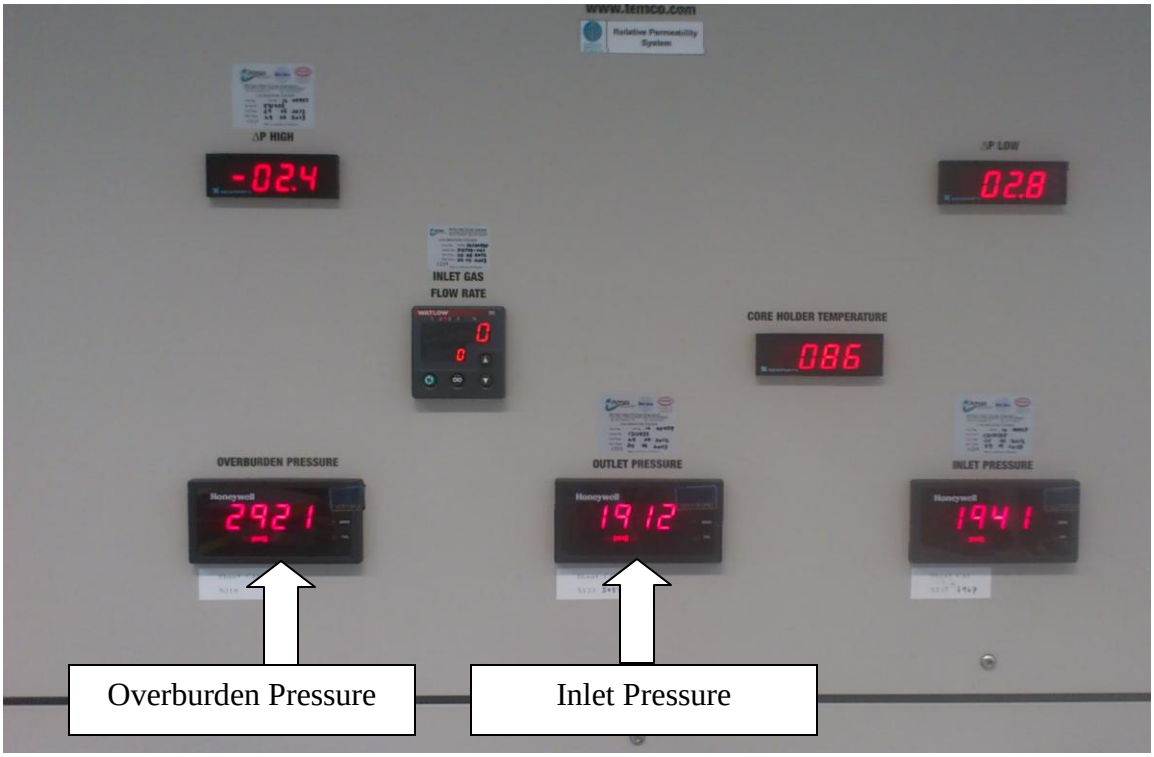


Figure 22 Pressure Monitoring

Throughout the whole core flooding test, the test is being ensured to run under the temperature of 85 ℃. This is because Dulang oil is very waxy in room temperature. The oil will be stuck inside the machine if it is run under room temperature. For this reason, the oil being produced at the outlet is very waxy. Heat need to be added to the flow lines from time to time, so that the oil can flow smoothly. The waxy Dulang oil can be seen in the *Figure 23*. The oil will be in liquid form after it is being heated up.

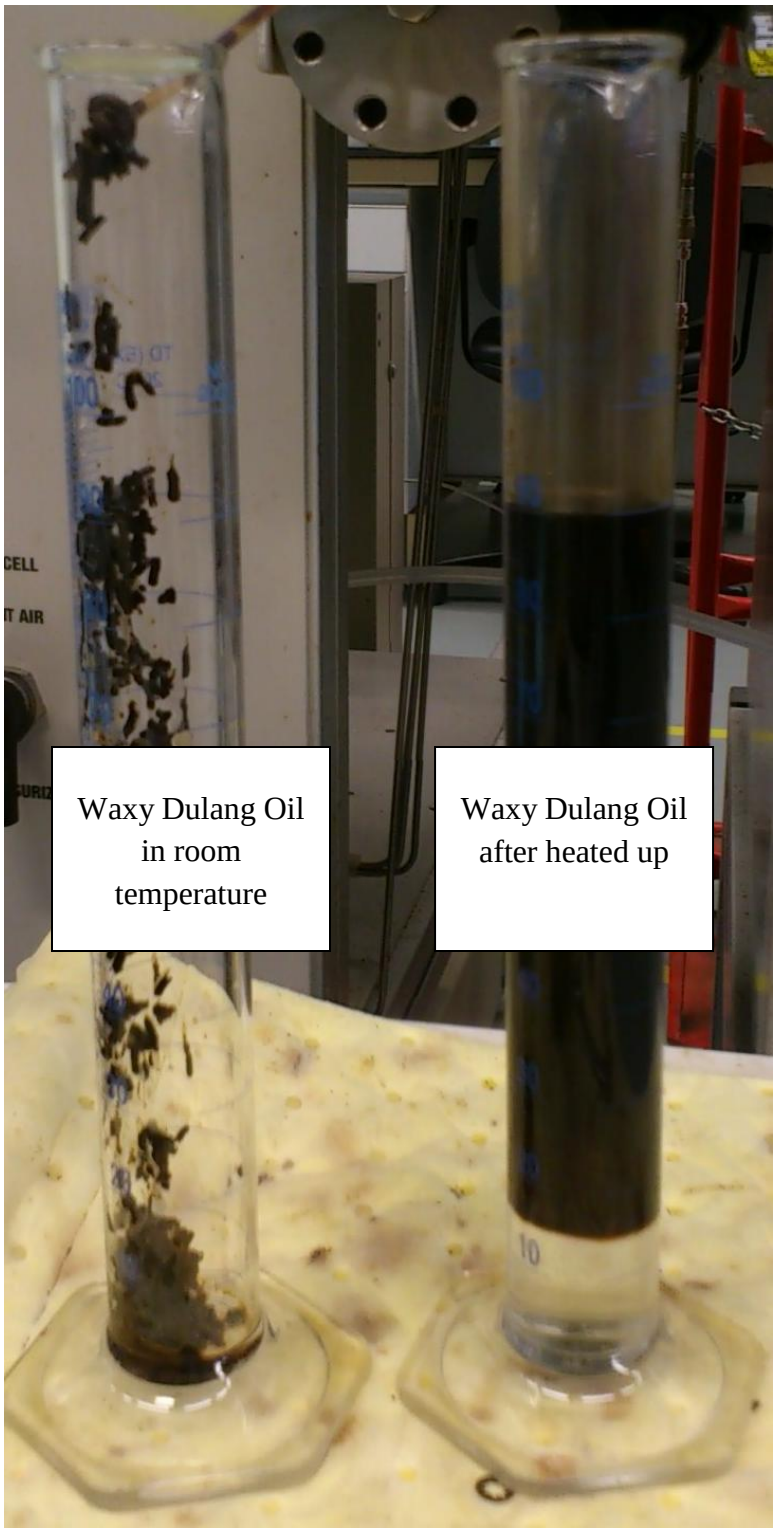


Figure 23 Oil Production

4.4 Cost analysis

Table 11 List of price for the chemicals

Chemical	Price per bottle	Price per gram / ml
1-Bromohexane	RM 99.50 (100 gram)	RM 1.00
Dioctyl Sulfosuccinate, Sodium Salt	RM 356.50 (100 gram)	RM 3.57
1-Methylimidazole	RM 510.00 (100 ml)	RM 5.10

Table 12 List of price for chemicals used to produced 11.269 gram of [HMIM][DOSS]

Chemical	Chemical Price
1-Bromohexane	RM 9.85 (9.9 gram)
Dioctyl Sulfosuccinate, Sodium Salt	RM 30.70 (8.4 gram)
1-Methylimidazole	RM 20.30 (398 ml)
Total	**RM 60.85**

While comparing the price of the synthesized IL to the available surfactant being used, the following research can be found. Depending upon the field properties wand water salinity, a typical 2% active lignin-based surfactant will cost between $2.30 and $3.50 per barrel injected and will recover between 0.6 bbl and 1.6 bbl of oil per barrel of surfactant injected in a field-scale project. (DeBons, 2002).

Converting lab scale to field scale, the cost of synthesized IL will be approximately $2.94 per barrel injected. However, the amount of oil to be recovered is unable to be converted from lab scale to field scale due to some of the field uncertainties.

Chapter 5: Conclusion and Recommendation

5.1 Conclusion

The ionic liquid product, [HMIM][DOSS] is manage to be produced. [HMIM][DOSS] has been synthesized while being analyzed. It has very high water content and it is very far deviated from the theoretical range. This might due to the reason that the sample was exposed to atmospheric moisture for a long time.

The low IFT value of IL is able to reduce the surface tension between the oil and the rock. Consequently, it can change the wettability of reservoir from oil wet to water wet, and hence improve oil recovery.

It is observed that [HMIM][DOSS] has no transition state and it is thermally stable. It is pure and free from any starting material. The IL is thermally stable up to 257.67 ℃ with complete decomposition 335 ℃. This high thermal stability is suitable to be used as an EOR agent.

While running for the application of EOR test using the synthesized ionic liquids, the properties of the core must first be known. The porosity and permeability of the two usable cores are being measured and recorded. The cores that were used are the Berea sandstone.

The result of the core flooding can be seen from the *Table 11* below.

Table 13 Oil Recovery Factor

RF for Secondary Flooding, %	33.083
RF for Tertiary Flooding, %	12.500
Total RF, %	45.583

Theoretically EOR can achieve RF of 10% to 20%. Since [HMIM][DOSS] is able to recovery 12.5% of oil in lab scale, it is generally can be taken into consideration to be used as an alternative EOR agent.

5.2 Recommendations for Future Work

There are a few recommendations can be listed to enhance the study in future. ILs synthesized should always be kept in the desiccators. This is to avoid atmosphere moisture from altering the chemical properties. Preparation of extra amount of IL is advisable. This is because in later part of the study, a large number of IL is needed for core flooding. For instances, at least 1 litre of injection fluid is needed to run for one core flooding test.

On the other hand, compatibility test can be done before the core flooding test is carried. Different brine concentration and IL concentration are mixed with crude oil in the ratio of 4:6, and then these sets of fluids are being kept in the oven under the temperature of 85℃ for a period of time. In addition to this, the samples will be observed for any emulsion occurring. This is to optimize the performance of the EOR agent to be used and minimize the time spent.

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